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This thesis is a resumé of the work presented in detail in the following papers:

I. Hansson, M. and Lundgren, G.
"X-Ray Studies on a Hafnium Sulphate"
Acta Chem. Scand. 22 (1968) 1683.

II. Hansson, M.
"The Crystal Structure of $Hf(OH)_2SO_4H_2O$"
Acta Chem. Scand. 23 (1969) 3541.

III. Hansson, M.
"The Crystal Structure of $Zr(OH)_2SO_4H_2O$"
Acta Chem. Scand. To be published.

IV. Hansson, M.
"The Crystal Structure of $Hf(OH)_2SO_4$"
Acta Chem. Scand. To be published.

V. Hansson, M., Lundgren, G. and McWhan, D.B.
"The Crystal Structure of $Zr(OH)_2SO_4$"
Acta Chem. Scand. To be published.

VI. Hansson, M. and Mark, W.
"The Crystal Structure of a Basic Hafnium Chromate"
Acta Chem. Scand. To be published.

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Introduction

The hydrolysis of the small tetravalent zirconium and hafnium ions is known to occur readily, even in rather acid solutions. There is also abundant evidence in the literature to the effect that Zr(IV) and Hf(IV) species are polymerized in aqueous solution. These effects are exemplified by the formation of tetrameric $[M_4(OH)_8(H_2O)_{16}]^{8+}$ complexes in concentrated solutions of zirconyl and hafnyl halides, as shown by Muha and Vaughan in an X-ray investigation.[1] These results were in accordance with results obtained earlier by Zielen and Connick,[2] who found that the tri- and tetrameric species, $[Zr_3(OH)_4]^{8+}$ and $[Zr_4(OH)_8]^{8+}$, predominated in 1-2 M perchloric acid. Johnson and Kraus[3] had also shown, by means of ultracentrifugation, that the degree of polymerization lay between three and four in ~0.5-2 M hydrochloric acid solutions.

A direct verification of this ability to form polynuclear complexes containing hydroxide bridges has been provided by crystal structure determinations of some basic zirconium and hafnium compounds reported earlier and in this paper. In the structures of the halide compounds, the tetrameric units are preserved,[4] while in the sulfate, chromate and nitrate[5] compounds there seems to be a tendency to form linear complexes. This difference may be explained by the greater ability of the oxoanions, e.g. SO_4^{2-} and CrO_4^{2-}, to form bridges between the metal atoms, as is apparent from the structures investigated.

The chemistries of the elements Zr and Hf are often reported in the literature as being identical. There are, however, significant differences in their tendencies to hydrolyze[6,7] and polymerize[3] as well as in the stabilities of their sulfate

complex compounds.[6,8,9] This is reflected in the results obtained in this investigation and will be discussed later in connection with the syntheses performed. The differences in the behaviour of Zr and Hf ions in solution are usually assumed to be due to the fact that hafnium has a filled f-orbital, which might cause it to be somewhat larger than zirconium. No complete and accurate structural data for hafnium compounds have, however, hitherto been available to verify this assumption. In this paper, the crystal structures of some pairs of isomorphous zirconium and hafnium salts are reported. The results would instead suggest that Hf(IV) is smaller than Zr(IV), the lanthanide contraction thus presumably being more effective than previously supposed.

Preparative and analytical work

The hafnium and zirconium compounds belonging to the MeO_2--SO_3-H_2O system (Me = Hf, Zr), and the hafnium chromate were all prepared by means of hydrothermal hydrolysis.

HfO_2-SO_3-H_2O

The HfO_2-SO_3-H_2O system was investigated in the following way: After dissolving pure HfO_2 in boiling concentrated sulfuric acid, the solutions were evaporated slowly to dryness. The residues thus obtained were dissolved in water or dilute sulfuric acid, sealed in Pyrex glass tubes or in an autoclave (for temperatures above 200°C) and heated for 3-4 weeks. By systematically varying the acidity and the temperature, different hafnium sulfates and hafnium oxide sulfates were obtained, most of the phases being amorphous or unstable. Of the more than 100 samples

obtained only the more crystalline and stable products were investigated, and the results are listed in Table 1. Guinier powder photographs, rotation and Weissenberg films were recorded in order to provide information concerning the cell dimensions and symmetries. The formulae are based on analyses performed with a Mettler Recording Thermoanalyzer, using a high temperature furnace (max. temp. 1600°C) and a platinum micro crucible. The crystals chosen for structure determinations are indicated in the table.

As expected, the water content in the crystals with a SO_3:HfO_2 molar ratio of 1:1 decreases with increasing temperature. It is also worth noting that, if the temperature is held constant at about 100°C, the normal salt (No. 5) is obtained from the most acid solution, while the two basic compounds (Nos. 9, 10 and 11) crystallize from 0 - 0.1 M and 1.0 M sulfuric acid, respectively. Crystals with a higher SO_3:HfO_2 molar ratio are always obtained at room temperature. They are also formed at higher temperatures, when the amount of solution in the autoclave is sufficiently low for the acidity to increase appreciably on heating (No. 17). The HfO_2-SO_3-H_2O system is discussed in greater detail later in this paper.

$\underline{ZrO_2\text{-}SO_3\text{-}H_2O}$

The crystals of $Zr(OH)_2SO_4H_2O$ were prepared under conditions as much alike those for preparing the corresponding hafnium salt as possible, though the experiments with mixed hafnium and zirconium solutions (reported in paper III) indicated that the distribution factor for the crystals was in favour of Hf. This is in accordance with the differences observed for the hydrolysis of the two systems. The crystals of $Zr(OH)_2SO_4$

Table 1. Preparation of different hafnium sulfates.

No.	Temp. °C	$[H_2SO_4]M$ added to residue after evaporation	Formula	Crystal data
1	20	1	$Hf(SO_4)_2 \cdot 4H_2O$	Mon. 6.5, 26.0, 5.1, $\beta=116^o$
2	"	2	"	
3	"	4	"	
4	"	9	"	
5	100	9	"	
6	20	2	unstable, not analyzed	Orth. 12.8, 5.5, 5.8 Å
7	75	0 (water)	$Hf(OH)_2SO_4 \cdot 2H_2O$	Hex. 34.09, 17.66 Å
8	"	0.1	"	
9	100	0 (water)	"	
10	"	0.1	" (paper I)	
11	100	1	$Hf(OH)_2SO_4H_2O$	Mon. 6.47, 12.45, 6.80 Å $\beta=96.2^o$
12	150	1	"	
13	175-200	0.1	"	
14	"	1	"	
15	"	2	" (paper II)	
16	300	2	$Hf(OH)_2SO_4 \cdot H_2O$ + $Hf(OH)_2SO_4$	
17	300	2	$HfO_2 \cdot 1.7SO_3 \cdot 3.1H_2O$	Mon. 15.3, 11.9, 4.7 Å $\beta= 95^o$
18	325	2	$Hf(OH)_2SO_4$ (paper IV)	Orth. 11.09, 5.52, 6.65 Å

(paper V), for instance, were obtained at a lower temperature and from slightly more basic solutions than those required for the hafnium compound to crystallize (No. 18, Table 1). Some divergences in the chemistry of Zr and Hf have also been noticed by Russian chemists.[6] They carried out experiments on the stability of complex zirconium and hafnium compounds, using ion-exchange techniques, which showed large differences in the abilities of Hf and Zr to form complex sulfate compounds. $ZrSO_4^{2+}$ is reported to be about three times as stable as $HfSO_4^{2+}$ and the $Zr(SO_4)_2$ species about one and a half times as stable as $Hf(SO_4)_2$. It was also pointed out that the Hf^{4+} ion has a lower tendency to hydrolyze than the Zr^{4+} ion. This last feature had been noted earlier by Larsen and Gammill,[7] in a study of the precipitation of zirconium and hafnium hydroxides.

HfO_2-CrO_3-H_2O

The crystals of the hafnium chromate, $4HfO_2 \cdot 4.3CrO_3 \cdot 5.4H_2O$, were prepared from 1.5 g HfO_2 dissolved in sulfuric acid and evaporated as described above. The residue was dissolved in about 30 ml water and 2 - 5 g $K_2Cr_2O_7$ was added. A yellow precipitate was obtained which ought to correspond to the amorphous zirconium chromate, "$ZrOCrO_4$", mentioned by Lundgren[10] and Mark[11] in their investigations of the ZrO_2-CrO_3-H_2O system. Hydrothermal reaction of this amorphous hafnium chromate with a 10 M chromium trioxide solution at 165° yielded a small amount of red crystals. The chromium and hafnium contents in the crystals were determined by electron probe microanalysis.

Crystallographic Investigation

A brief outline of the methods and computer programs used to determine the crystal structures is presented in this thesis, while detailed accounts of the investigations are to be found in Papers I-VI.

Accurate cell dimensions were determined from Guinier powder photographs and refined by least squares calculations with the program POWDER.[12] The resulting cell parameters for all the structures are given in Table 2.

I. $Hf(OH)_2SO_4H_2O$

Intensity data were collected with an automatic single crystal diffractometer (Philips PAILRED) using MoKα radiation, with the a-axis of the crystal as rotation axis. The crystal was mounted in a capillary since most of the phases obtained in the synthesis appeared to be efflorescent or hygroscopic in air. Those crystals, however, which were obtained at 200°C from about 2 M sulfate solutions, were stable in sealed capillaries. For $Hf(OH)_2SO_4\ H_2O$ a data set of 1467 independent reflexions was used in the calculation of a Patterson synthesis and subsequent Fourier calculations. In the final refinement 53 parameters consisting of scale factors, positional and anisotropic thermal parameters were calculated. After correction had been made for absorption (μ = 207 cm^{-1} for MoKα radiation), a final R value of 0.066 was obtained. The programs used for the absorption correction and the refinement were DATAP2 and LALS.[13] The differences in peak heights observed in Fourier maps based on calculated and observed structure factors, respectively, are mainly due to the fact that no correction was per-

Table 2. Unit cell dimensions for the compounds investigated.

	Symmetry	a (Å)	b (Å)	c (Å)	β	V (Å^3)	Z
$Hf(OH)_2SO_4H_2O$	Mon.	6.4652(4)	12.4476(10)	6.7973(5)	96.198(4)°	543.8	4
$Zr(OH)_2SO_4H_2O$	"	6.4969(4)	12.4598(10)	6.8262(4)	96.311(4)°	549.2	4
$Hf(OH)_2SO_4$	Orth.	11.0850(12)	5.5170(4)	6.6474(7)		406.5	4
$Zr(OH)_2SO_4$	"	11.1034(18)	5.5467(10)	6.6600(12)		410.2	4
$Hf(OH)_2SO_4 \cdot 2H_2O$	Hex.	34.090(16)	34.090(16)	17.664(7)		17 750	~108
$4HfO_2 \cdot 4.3CrO_3 \cdot 5.4H_2O$	Orth.	11.541	13.587	6.847		1073.7	2

Calculated standard deviations (in the last decimal(s)) are given in parentheses in the table.

formed for extinction effects in this crystal, nor were the scattering factors for Hf and S corrected for anomalous dispersion. That this is the main reason is confirmed by results obtained for the isomorphous zirconium compound, the difference density map calculated before the above-mentioned corrections were carried out showing exactly the same discrepancies between $\underline{F}_c$ and $\underline{F}_o$. An electron difference density calculation with the program FFT,[13] which handles corrections for extinction effects, gave, however, only negligible rest peaks around the zirconium atoms.

II. $Zr(OH)_2SO_4H_2O$

The data collection for $Zr(OH)_2SO_4H_2O$ was performed in the same way as for the corresponding hafnium salt. The atomic parameters were deduced from a Patterson synthesis and a subsequent electron density calculation using a data set of 1050 reflexions. Corrections were applied for absorption and extinction effects after which the mean values of $\underline{F}_{0k\underline{l}}$ and $\underline{F}_{0k\bar{\underline{l}}}$ could be calculated, since the crystal was very symmetric in shape. A data set of 986 independent reflexions was thus used in the final refinement with the program LINUS.[13] The 43 parameters refined in the last calculation were: atomic positions, including anisotropic parameters, and an isotropic secondary extinction factor. An $\underline{R}$ value of 0.060 was obtained when the scattering factors for Zr and S were corrected for anomalous dispersion.

III. $Hf(OH)_2SO_4$

Three-dimensional X-ray data for $Hf(OH)_2SO_4$ were collected with a Philips automatic four-circle diffractometer, PW 1100. 405 independent reflexions, registered with $Cu\underline{K}\alpha$ radiation,

were used in the final refinement of the structure. The linear absorption coefficient was rather high, $\mu_{CuK\alpha} = 530\ cm^{-1}$, and corrections were performed for absorption as well as for extinction, using the programs DATAPH and LINUS,[13] respectively. A final refinement of 43 parameters, including anisotropic thermal vibrations, yielded an R value of 0.055 when the atomic scattering factors for Hf and S were corrected for anomalous dispersion using the real component only.

IV. $Zr(OH)_2SO_4$

Weissenberg data for the layers hk0 and h0l-h3l for the isomorphous zirconium compound had been recorded earlier by McWhan with CuKα radiation, and a preliminary outline of the structure was reported in 1966.[14] It was, however, desirable to obtain more detailed information concerning the structure for comparison with the hafnium compound. The structure has therefore been refined further and the results are to be published. The 343 reflexions, measured by comparison with a logarithmic scale, were used in the refinement of 25 parameters including scale factors and atomic and isotropic thermal parameters. As no information was available concerning the crystal used in the data collection, no correction could be performed for absorption effects. The linear absorption coefficient ($\mu = 276\ cm^{-1}$) and the final R value of 0.13, indicate that such a correction had been desirable.

V. $Hf(OH)_2SO_4 \cdot 2H_2O$

Weissenberg and precession photographs corresponding to the layers hk0-hk9 and 0kl-2kl, respectively, were recorded using CuKα radiation in order to elucidate the symmetry of the

crystals. The data obtained were in accordance with the space groups No. 176 $\underline{P6_3/m}$ and No. 173 $\underline{P6_3}$.[15] Because of the large unit cell the formula of the compound could not be determined unambiguously, but the experimental density obtained and the volume of the cell indicate 108 formula units of $Hf(OH)_2SO_4(H_2O)_2$ per unit cell. This implies some sort of disorder in the structure and since this was the first compound investigated in the series of hafnium salts only a three-dimensional Patterson synthesis based on visually estimated intensities, was calculated. It is hoped that with the help of the structures determined it will be possible to locate the heavy atoms, but as discussed later in this thesis it is not yet possible to make any definite predictions concerning the structure.

VI. ~ $Hf_4(OH)_8(CrO_4)_4H_2O$

Intensity data were collected for $\underline{hkl}$ and $\underline{\bar{h}kl}$, $\underline{k} = 2\underline{n}$, with an automatic single crystal diffractometer (Philips PAILRED) using $\underline{MoK\alpha}$ radiation. Due to the positions of the Hf atoms in the structure, reflexions with $\underline{k}$ odd are very weak and, in order to obtain a better accuracy, these were registered using multiple film Weissenberg techniques and $\underline{CuK\alpha}$ radiation. The 311 reflexions from the layer lines $\underline{h1l}$-$\underline{h9l}$, $\underline{k} = 2\underline{n}+1$, thus obtained were estimated visually.

The positional parameters for the Hf atoms were assumed to be the same as for Zr in $Zr_4(OH)_6(CrO_4)_5H_2O$.[11] A structure factor calculation based on these parameters was used to put the two data sets (1507 reflexions in all) on to approximately the same scale. Refinement of positional and isotropic thermal parameters, together with the scale factors, was performed with the program BLOCK,[13] different occupation numbers being assigned

to a chromate group and a water molecule statistically distributed between the same point position. The best fit with the experimental data indicated a formula of $4HfO_2 4.3CrO_3 5.4H_2O$, which is in accordance with the results obtained by electron probe microanalysis. The final refinement of 58 parameters, with the program LALS,[13] was based on a data set consisting of 507 strong structure factors with $\underline{k} = 2\underline{n}$ (mean values of $F_{\underline{hkl}}$ and $F_{\underline{\bar{h}\bar{k}\bar{l}}}$ calculated for those reflections obtained twice) and 311 weak structure factors with $\underline{k} = 2\underline{n}+1$. The final $\underline{R}$ value based on all the 818 structure factors was 0.061, values of 0.045 and 0.158 being obtained for the strong and weak structure factors, respectively.

Description of the structures

The main structural features of the compounds investigated are given below; further details are given in Papers II-VI.

Some interatomic distances and angles in the structures are given in Tables 3 and 4 in such a way as to facilitate a comparison mutually and with wome related compounds.

I,II. $Hf(OH)_2SO_4H_2O$, $Zr(OH)_2SO_4H_2O$

In these structures the metal atoms form zigzag rows and are joined by double hydroxide bridges, thus constituting infinite chains with the formula $[Me(OH)_2]_{\underline{n}}^{2\underline{n}+}$. These almost planar chains, lying in the $\underline{yz}$ plane, are connected in the $\underline{x}$ direction by sulfate groups, each of which is in contact with two metal atoms in different chains. Each metal atom is pentagonal bipyramidally coordinated by the oxygen atom of a water molecule, four hydroxide and two sulphate oxygen atoms

Table 3. Distances and angles within the MeO_7 pentagonal bipyramids in structures II, III and VI. For comparison the values for $Zr_4(OH)_6(CrO_4)_5H_2O$,[11] $Zr(OH)_2CrO_4$[16] and $ZrO_2 \cdot 2MoO_3 \cdot 3H_2O$[17] are included. Some intermetallic distances are also given.

Compound	Hf(Zr)-O distances (Å)			O-Hf(Zr)-O angles (°)			O-O distances (Å)				Hf(Zr)-Hf(Zr) distances (Å)
	eq.	av. eq.	axial	ax.-ax.	ax.-eq.	eq.-eq.	eq.-eq.	av.	eq.-ax.	av.	
$f(OH)_2SO_4H_2O$	2.10_0 2.15_1 2.18_2	2.13_6	2.07_6	177.0	87.0-93.5	66.6-78.9	2.33_4-2.66_9	2.51_3	2.91_1-3.04_2	2.97_8	3.553
$r(OH)_2SO_4H_2O$	2.107 2.170 2.190	2.149	2.112	175.1	87.5-95.0	66.9-78.4	2.35_9-2.66_2	2.52_7	2.95_2-3.11_1	3.01_2	3.568
$f_4(OH)_8(CrO_4)_4H_2O$	Hf_1 2.24 2.09 2.12 2.25 2.03	2.12_6	2.10	167	84.7-96.7	66-77	2.34-2.70	2.52	2.82-3.13	3.00	3.545-3.579
	Hf_2 2.13 2.21 2.08 2.25 2.01	2.13_6	2.08	176	87.9-91.9	66-78	2.33-2.78	2.52	2.92-3.07	2.98	

Table 3. Continued.

Compound	Hf(Zr)-O distances (Å)			O-Hf(Zr)-O angles (°)			O-O distances (Å)				Hf(Zr)-Hf(Zr) distances (Å)
	eq.	av. eq.	axial	ax.-ax.	ax.-eq.	eq.-eq.	eq.-eq.	av.	eq.-ax.	av.	
$Zr_4(OH)_6(CrO_4)_5H_2O$	Zr_1 2.19_1 2.16_0 2.17_2 2.13_8 2.17_9	2.16_8	2.069	171.8	86.0-93.6	66.4-79.5	2.37_4-2.78_1	2.54_6	2.90_5-3.09_7	2.99_8	3.564-3.641
	Zr_2 2.21_6 2.14_4 2.15_7 2.16_9 2.13_7	2.16_5	2.079	172.2	86.1-93.1	66.8-78.7	2.37_4-2.71_4	2.54_3	2.93_4-3.06_2	3.00_0	
$Zr(OH)_2CrO_4$	2.26 2.12 2.17	2.17	2.08	166.2	83.1-95.4	66.2-78.4	2.35-2.69	2.55	2.88-3.11	3.00	3.646
$ZrO_2 \cdot 2MoO_3 \cdot 3H_2O$	2.14_1 2.17_3 2.17_5	2.16_7	2.08_8	173.9	87.1-93.1	69.1-74.4	2.44_7-2.62_9	2.54_8	2.93_8-3.07_5	3.01_1	

Table 4. Distances and angles within the MeO_8 antiprisms in structures IV and V compared with those in $Zr(SO_4)_2 \cdot 4H_2O$[18] and Zr(acetylacetonate)$_4$.[19] Values for the most favourable model (MF) according to Hoard and Silverton[20] are included.

	$Hf(OH)_2SO_4$	$Zr(OH)_2SO_4$	$Zr(SO_4)_2 \cdot 4H_2O$	Zr(acetylacetonate)$_4$	MF
Me-O distances (Å)	2.14 (OH) (2x)	2.14 (OH) (2x)	2.18 (SO_4)	2.22	
	2.11 " "	2.16 " "		2.20	
	2.25 (SO_4)	2.25 (SO_4)	2.18 (H_2O)	2.18	
	2.26 "	2.26 "		2.19	
	2.20 " (2x)	2.18 "			
Mean Me-O distance (Å)	2.17_4	2.18_5	2.18_0	2.19_8	2.18
O-O distances (Å)					
s (square faces)	2.76	2.74	2.62	2.67 (mean)	2.59
	2.30	2.40			
	2.60	2.63	2.53	2.59 (mean)	
	2.53	2.48			
l (triangular faces)	2.74	2.74	2.72	2.69	2.75
	2.73	2.70	2.86	2.81	
	2.90	2.86	2.65	2.72	
	2.92	3.01			
l/s	1.11	1.11	1.07	1.04	1.06
Me-Me distance (Å)	3.562	3.576			

(cf. Fig. 1).

The structure can be described in terms of layers, parallel to the xz plane, in which the metal atoms are bridged in one direction by double hydroxide bridges and in the other by sulfate groups. These layers are held together mainly by hydrogen bonds between the water molecules and the non-connecting sulfate oxygen atoms.

III, IV. $Hf(OH)_2SO_4$, $Zr(OH)_2SO_4$

As in $Hf(OH)_2SO_4H_2O$ and $Zr(OH)_2SO_4H_2O$, the basic units in these structures are $[Me(OH)_2]_n^{2n+}$ chains, but the arrangement of atoms within the chains differs in the two structure types. In $Hf(OH)_2SO_4$ and $Zr(OH)_2SO_4$ the hydroxide ions form two parallel rows with the metal atoms situated on alternate sides of these rows. The chains are linked together by sulfate ions to form a three-dimensional arrangement so that each of the sulfate groups is in contact with three different chains.

There are four oxygen atoms, belonging to different sulfate groups, bonded to each metal atom, and, together with the bridging hydroxide oxygen atoms, these constitute a distorted square antiprismatic arrangement (cf. Fig. 2). The sulfate tetrahedra share their four vertices with four ZrO_8 antiprisms. Two different chains of coordination polyhedra with some of the chain-connecting sulfate groups are outlined in perspective in Fig. 3.

VI. ~ $Hf_4(OH)_8(CrO_4)_4 \cdot H_2O$

This structure is built up from chains with the approximate composition $[Hf_4(OH)_6CrO_4]_n^{8n+}$. The hafnium atoms are joined by double oxygen bridges situated in the same plane thus forming

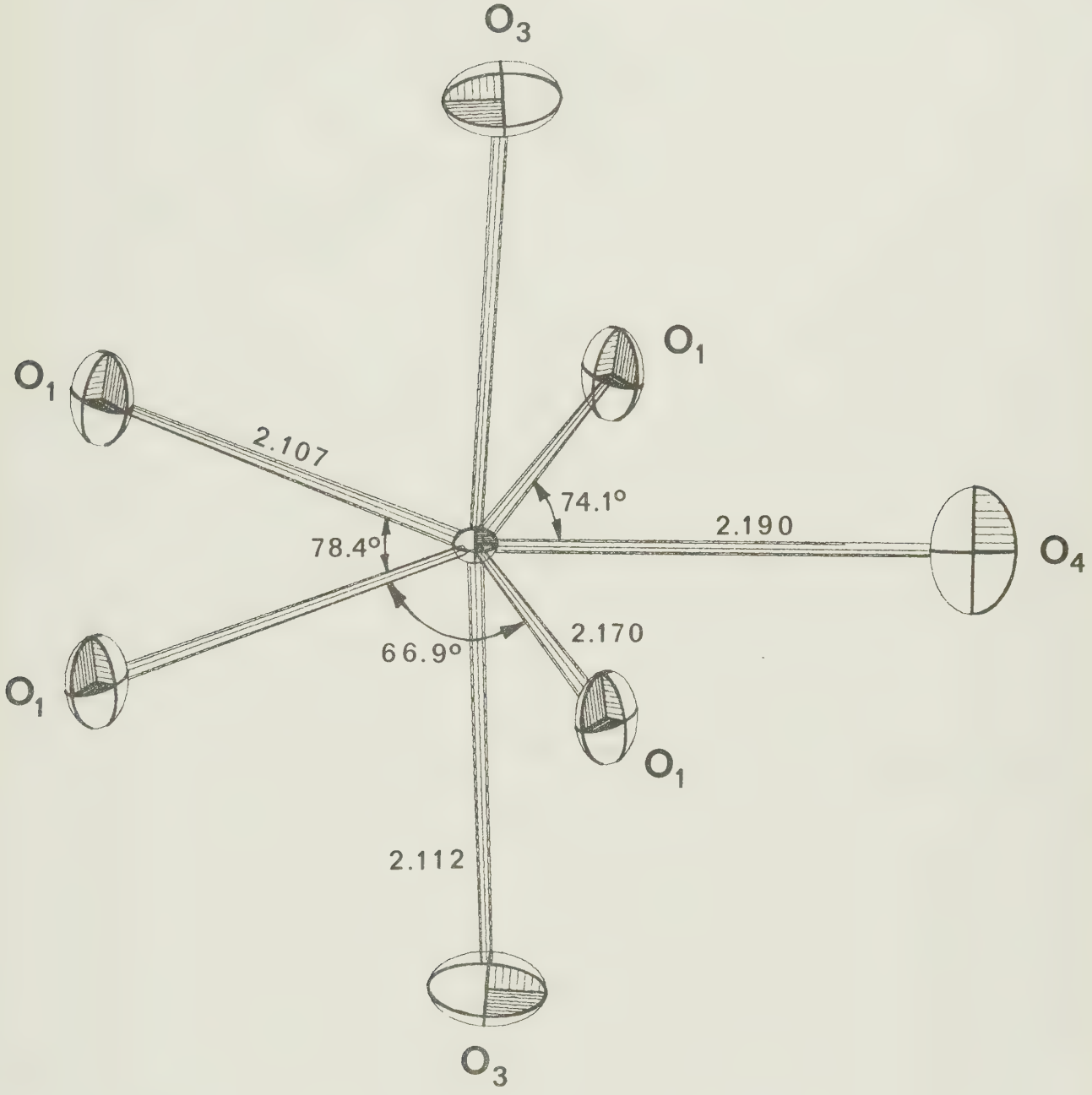

Fig. 1. The oxygen coordination of Zr in $Zr(OH)_2SO_4H_2O$. The Zr-O distances (in Å), some O-Zr-O bond angles and anisotropic thermal vibrations are indicated (probability level: 50 %).

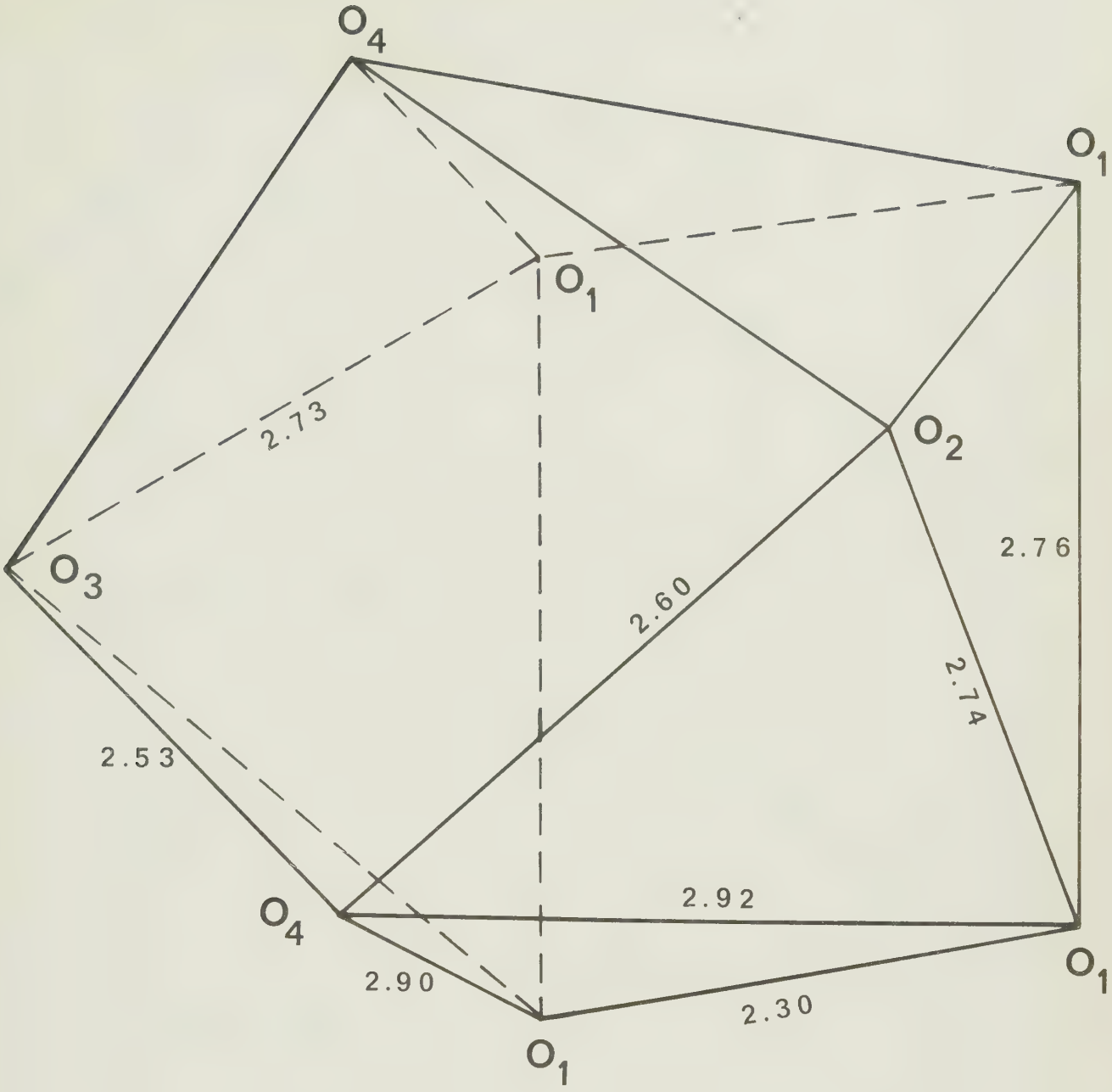

Fig. 2. Antiprismatic configuration of oxygen atoms about hafnium in $Hf(OH)_2SO_4$. (Distances in Å.)

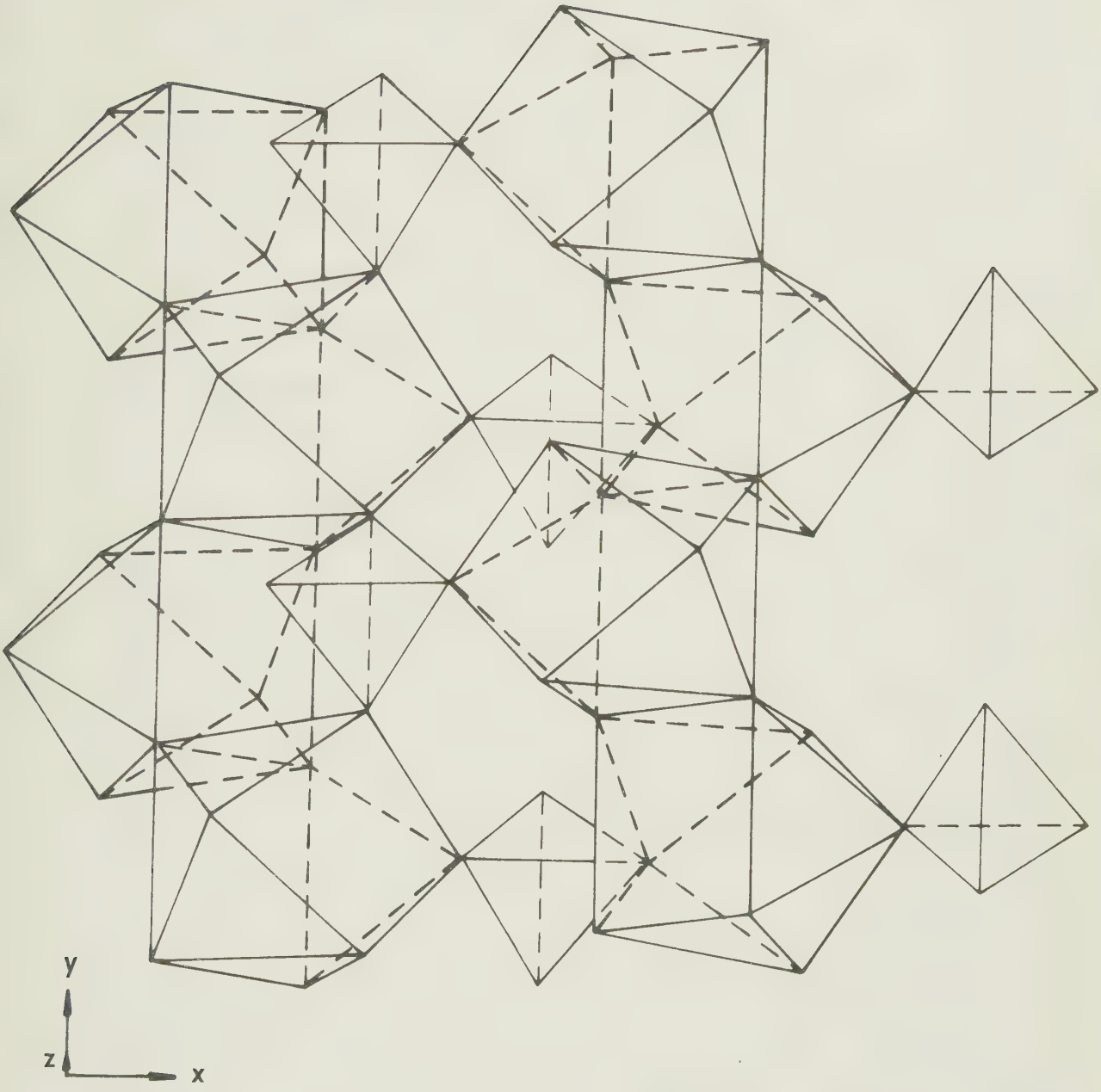

Fig. 3. Parts of two infinite chains of distorted square antiprisms connected by sulfate groups.

planar chains as in Structures II and III. There are a further three oxygen atoms coordinated to each metal atom, the latter thus being surrounded by seven oxygen atoms situated at the vertices of a pentagonal bipyramid. Three vertices of each bipyramid, i.e. one equatorial and two axial, are also vertices of three different chromate tetrahedra. These chromate groups connect the chains (running in the y direction) in both the x and z directions, since each tetrahedron belongs to three different chains.

The chromate groups which belong to one chain only are considered to be randomly distributed between the four equivalent positions available in each unit cell. The occupation numbers of these chromium atoms are stated to be 0.14 only, according to the results of the electron probe microanalysis and to the best fit with the observed data. In the holes in the structure, arising through the non-occupation of all available positions by CrO_4 tetrahedra, there are approximately two molecules of interstitial water per unit cell.

In Fig. 4 two chains of bipyramids are shown without the condensed CrO_4 group. The connection of the chains by means of chromate tetrahedra in the z direction is shown, whereas the connection in the x direction is accomplished through the marked chromate oxygen atoms. Approximately one formula unit is shown in Fig. 5.

Discussion

A characteristic feature of the structures described above is the chains consisting of metal atoms joined by double hydroxide bridges. Although some of the hydroxide groups have

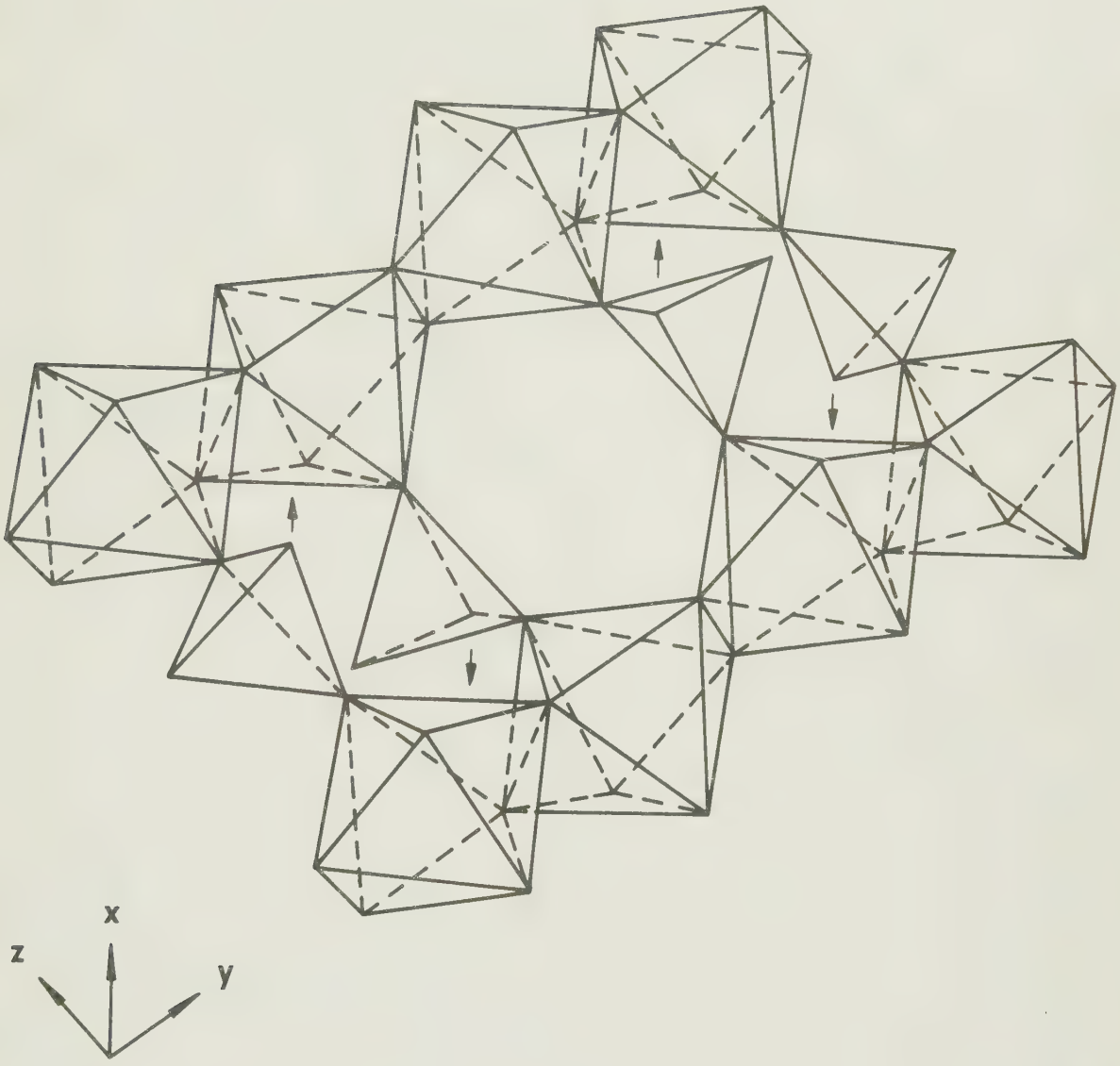

Fig. 4. Connection of the pentagonal bipyramids in two Hf-O chains by Cr-O tetrahedra. Only the oxygen atoms are depicted. The arrows indicate in which way the chains are connected to other chains in the $\underline{x}$ direction.

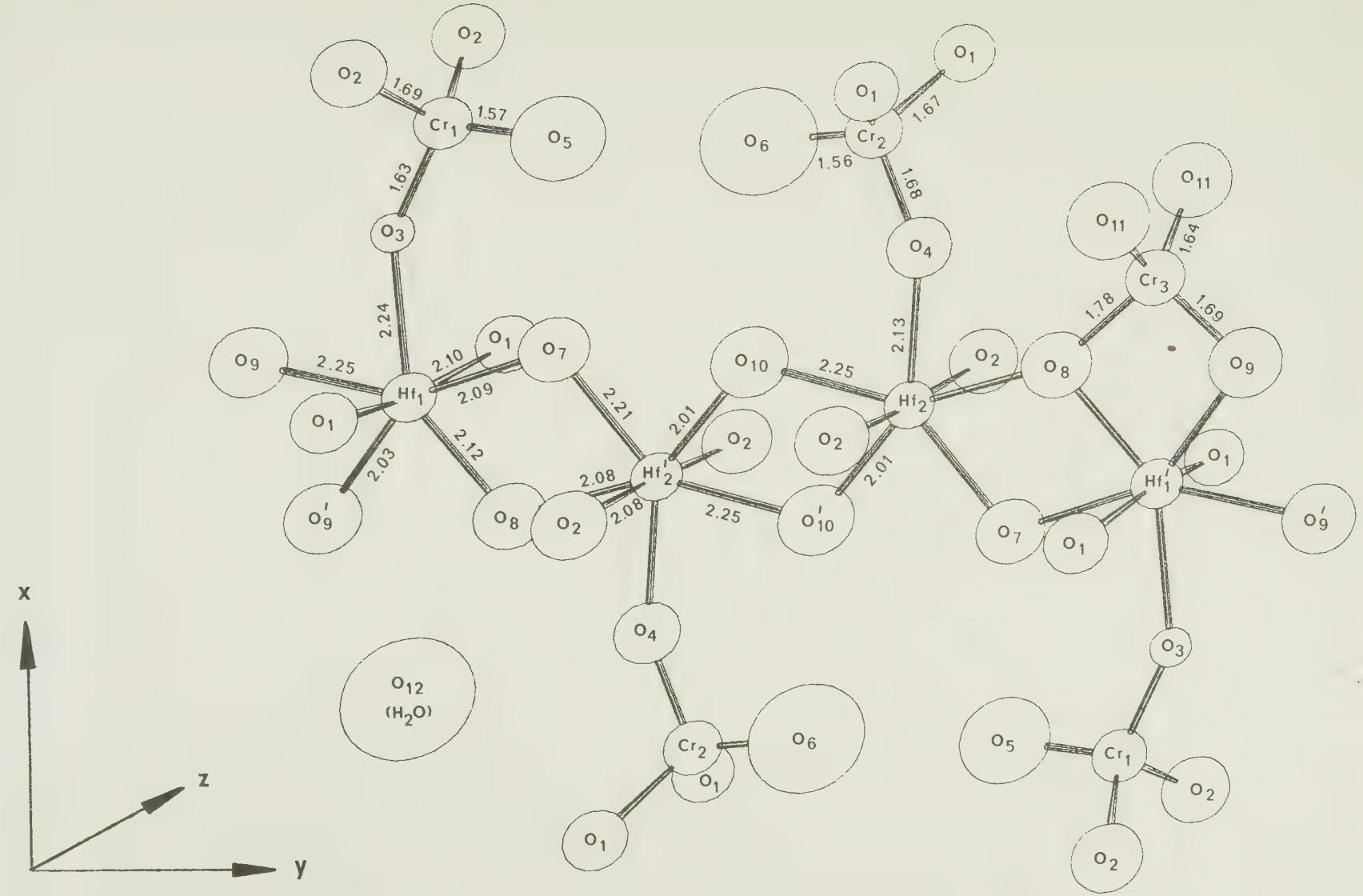

Fig. 5. One approximate formula unit of $4HfO_2 \cdot 4.3CrO_3 \cdot 5.4H_2O$ shown in perspective. The thermal motions are outlined as spheres and the distances are given in Å.

been displaced by chromate oxygen atoms in the hafnium chromate complex, this structure can also be regarded as consisting basically of $[Me(OH)_2]_n^{2n+}$ chains.

Two main types of arrangement of metal and hydroxide ions have been found within the infinite chains in basic Zr and Hf salts, as in some related compounds. In the structures of $Me(OH)_2SO_4H_2O$,[II,III] where Me = Zr and Hf, $Zr_4(OH)_6(CrO_4)_5H_2O$[11] and $Hf_4(OH)_8(CrO_4)_4H_2O$[VI] there are planar arrangements while in the isomorphous sulfates $Me(OH)_2SO_4$, Me = Hf,[IV] Zr,[V] Th,[21] U,[22] and in $Th(OH)_2CrO_4H_2O$[23] the metal atoms are situated on alternate sides of two parallel rows of hydroxide ions (cf. Fig. 3). The type of chain adopted by a particular compound is of importance for the coordination number of the metal atom. In the structures containing planar chains, the metal atoms are 7-coordinated, while in the other structures they are 8-coordinated. This would seem to be a consequence of the more compact packing in the $Me(OH)_2SO_4$, which contains no water molecules, causing the metal atoms to be displaced out of the plane of the hydroxide oxygen atoms. A square is thus formed on one side of the metal atom by the hydroxide ions, while on the other side there is a square consisting of sulfate oxygen atoms. In $Me(OH)_2SO_4H_2O$ the hydroxide square is distorted to allow a water molecule to complete a pentagon. A favourable packing of the atomic groups thus seems to be of decisive importance in the establishment of a particular configuration around the metal atom.

This is also apparent on comparison of the coordination polyhedra found in the chromate system. In $Zr_4(OH)_6(CrO_4)_5H_2O$[11] and in Structure VI the pentagonal bipyramid is fairly similar to the dodecahedron in $Zr(OH)_2CrO_4$,[16] since both can be de-

scribed in terms of a trapezoid. In the dodecahedron, two such trapezoids are perpendicular to each other, while in the bipyramid a trapezoid is perpendicular to a triangle. If a chromate tetrahedron sharing an edge with a dodecahedron is tilted so that only one of the vertices is part of the coordination polyhedron, the metal atom will be 7-coordinated.

Several authors have dealt extensively with 7- and 8--coordination in order to elucidate the most favourable polyhedra in highly coordinated molecular structures. This is discussed in more detail in Paper II for the arrangement of seven atoms around a central atom. Those conclusions which can be drawn are that the energy differences between the idealized models are very small and interconversions between them are quite easily established. However, the treatment is rather limited, and taking polymerization and packing restrictions into consideration, the forces excerted on the coordinated atoms, in addition to the interparticle forces must vary considerably from one compound to another. Thus it is not possible to predict *a priori* which of the coordination polyhedra a particular complex will assume. For seven-coordinated Zr and Hf compounds D_{5h} symmetry, *i.e.* a pentagonal bipyramid, is the most common, while C_{2v} and C_{3v} symmetries have been found in other metal ion complexes.[24]

Eight-coordination has been discussed by Duffey[25] on the basis of valence bond theory taking into consideration possible orbital overlaps solely from symmetry arguments. The only three configurations of eight hybrid orbitals which can be derived from *s*, *p* and *d* orbitals alone are those with symmetry D_{4d}, D_{2d} or C_{2v}. The last is, however, a hybrid of the D_{4d} and D_{2d} geometries and has only been established for $[Eu(acac)_3(H_2O)_2]H_2O$.[26]

The dodecahedron (D_{2d}-$\bar{4}2m$) and the square antiprism (D_{4d}-$\bar{8}2m$) are the most common arrangements of eight ligands about a central atom. They can both be deduced from a cubic arrangement but are favoured because a cubic configuration would involve greater inter-ligand steric interactions. Moreover, only seven hybrid orbitals of cubic symmetry can be generated, unless f orbitals are included. Recently, one type of complex with cubic symmetry has been reported to exist: the $[MeF_8]^{3-}$ anion in Na_3MeF_8 (Me = U,Pa,Np).[27] Except for these complexes and some uranyl compounds, all octa-coordinate molecular species seem to have either the dodecahedral or the square antiprismatic structure. Attempts have been made by Hoard and Silverton,[20] and later by Kepert,[28] to quantitatively formulate the conditions favouring the formation of the antiprism or the dodecahedron. Their results are in accordance with those obtained by Duffey[25] in the calculation of the orbital strengths for the different symmetries. It seems impossible also for 8-coordination to predict the geometry expected for a particular compound because the stabilization of either polyhedron can be attributed to several different effects. In a review of high coordination numbers, Muetterties and Wright[29] have discussed both 7- and 8--coordination quite exhaustively, whereas Lippard[30] has dealt with eight-coordination only. The importance of metal-ligand π-bonding and ligand constraints is under investigation by Hamilton et. al.[31]

There thus seem to be insignificant differences between the various parameters favouring a particular stereoisomer for the coordination numbers of seven and eight, respectively. A favourable packing in the chain structures of Zr and Hf is of decisive importance for both a particular coordination number

and the steric configuration. In fact there is a chromate complex,[16] $Zr(OH)_2CrO_4$, built up from infinite nets, which contains both 7- and 8-coordinated metal atoms. In addition there is a distortion of the square faces in $Me(OH)_2SO_4$, one is *e.g.* somewhat puckered, which can be interpreted in terms of an approach towards dodecahedral symmetry.

As a consequence of the different coordination numbers in $Me(OH)_2SO_4H_2O$ and $Me(OH)_2SO_4$, respectively, the Me-Me distances as well as the mean Me-O distances in the former complexes are significantly shorter than those in the corresponding salt of the latter type (*cf.* Table 5). In addition, the mean value for the metal-oxygen distances in the hepta-coordinated hafnium chromate seems to be in accordance with the mean Hf-O value in $Hf(OH)_2SO_4H_2O$.

The distortions of the polyhedra in the various complexes are mainly due to the presence of the double hydroxide bridges between the metal atoms. This arrangement causes the metal atoms in the antiprisms to be located closer to the "square" of hydroxide ions, and the short distances between the oxygen atoms in the bridges cause an effective compression of this "square". This is particularly noticeable in $Hf(OH)_2SO_4$ (*cf.* Fig. 2) which has the shortest O-O bridge distance (2.30 $\pm$ $\pm$ 0.02 Å) yet reported for these types of complexes.

A considerable deviation from the ideal D_{5h} symmetry is found for the pentagonal bipyramid in the hafnium chromate complex. As can be seen from Fig. 5 the distances between hafnium and the bridging oxygen atoms are alternately long and short. This may be due to the short Hf-Hf distance, av. 3.56_2 Å, compared with the corresponding Zr-Zr distance, av. 3.597 Å. in $Zr_4(OH)_6(CrO_4)_5H_2O$,[11] which results in a displacement of the

Table 5. Distances within the chains in structures II-VI and in $Zr_4(OH)_6(CrO_4)_5H_2O$.[11]

Compound	Me–Me (Å)	av. Me–O (Å)	O–O in the bridges (Å)
$Hf(OH)_2SO_4H_2O$	3.553	2.11_9	2.334 ± 0.018
$Zr(OH)_2SO_4H_2O$	3.568	2.138	2.359 ± 0.011
$Hf(OH)_2SO_4$	3.562	2.17_4	2.303 ± 0.024
$Zr(OH)_2SO_4$	3.576	2.18_5	2.397 ± 0.030
$Hf_4(OH)_8(CrO_4)_4H_2O$	av. 3.562	Hf_1–O : 2.13 Hf_2–O : 2.12	2.34, 2.33, 2.34
$Zr_4(OH)_6(CrO_4)_5H_2O$	av. 3.597	Zr_1–O : 2.140 Zr_2–O : 2.140	2.37, 2.38, 2.40

bridging oxygen atoms in opposite directions, the O-Me-O angles being kept constant, in order to prevent too close a contact between these oxygen atoms. Moreover, there may be ligand constraints in the structure due to repulsion between two oxygen atoms, at a distance of 2.73 Å from one another, belonging to different chromate groups.

In Table 6 the distances and angles in the sulfate tetrahedra are listed, together with the values for $Zr_2(OH)_2(SO_4)_3(H_2O)_4$[14] and the normal tetrahydrate $Zr(SO_4)_2 4H_2O$.[18] The distortions from the ideal tetrahedral symmetry are in accordance with those usually found for sulfate groups sharing their oxygen atoms in different ways. In the normal zirconium sulfates, investigated by Bear and Mumme,[32] the maximum and minimum values for S-O distances were found to be 1.52 Å and 1.42 Å, respectively.

In the sulfate complexes the Hf-Hf distances within the chains are definitely shorter (by about 0.015 Å) than the corresponding zirconium distances, and the same significant difference is found for the chromate complexes. There would, moreover, seem to be a clear trend towards a shorter Hf-O distance compared with the corresponding Zr-O distance in comparable complexes (cf. Tables 3 and 4). These results suggest that Hf(IV) is smaller than Zr(IV) rather than vice versa as predicted.

Interpretation of the HfO_2-SO_3-H_2O system

When analyzing the different products listed in Table 1, it was noticed from the DTA curves that the endothermic reactions, which occurred when the water content was removed from

Table 6. Distances within the SO_4 tetrahedra in $Me(OH)_2SO_4H_2O$ and $Me(OH)_2SO_4$ compared with the values obtained for $Zr(SO_4)_2 4H_2O$[18] and $Zr_2(OH)_2(SO_4)_3(H_2O)_4$.[14]

	S-O (Å)	O-O (Å)	Angles (°)
II. $Hf(OH)_2SO_4H_2O$	1.44_7	2.40	111.7
	1.49_7	2.39	105.1
		2.43	108.5
		2.38	111.4
III. $Zr(OH)_2SO_4H_2O$	1.44_8	2.42	113.1
	1.48_0	2.38	106.6
		2.39	108.9
		2.37	109.6
IV. $Hf(OH)_2SO_4$	1.48	2.43	110.8
	1.47	2.36	107.7
	1.46	2.43	111.4
		2.37	107.7
V. $Zr(OH)_2SO_4$	1.45	2.37	107.8
	1.48	2.48	109.6
	1.52	2.46	112.4
		2.41	107.2
$Zr(SO_4)_2 \cdot 4H_2O$	1.44_3	2.37	112.5
	1.48_6	2.40	106.9
		2.37	107.7
		2.37	
$Zr_2(OH)_2(SO_4)_3(H_2O)_4$	1.46	2.38	
	1.45	2.34	
		2.36	
		2.48	
	1.44	2.35	
	1.49	2.37	
	1.48	2.37	
	1.44	2.42	

the samples, were registered at rather high temperatures for most of the compounds. As can be seen from Table 7, where the peaks in the DTA curves are listed, the water molecules, coordinated to the metal atom as OH^- or H_2O (paper II and IV), leave at the highest temperatures. Presumably the products Nos. 2 and 5, Table 7, also contain these more tightly bonded water molecules, corresponding to the smaller peaks at 300°C, as well as a larger amount of structurally different water of crystallization.

For $Hf(OH)_2SO_4 \cdot 2H_2O$ (No. 1, Table 7) the reactions corresponding to the water removal are seen to occur at much lower temperatures than for the other complexes. There was in fact a larger peak with its maximum at 115°C, together with a distinct shoulder at ~150°C. Since the reaction was not complete until about 300°C the structure may contain more firmly connected hydroxide groups as well. This would support the formula adopted.

A similar thermogravimetric investigation of a hafnium sulfate, corresponding to No. 2 in Table 2, has been reported by Vinarov and Kovalova,[33] and, on the basis of their interpretation of the curves obtained, the compound was formulated as $H_2HfO(SO_4)_2 \cdot 3H_2O$. The heating rate in their experiment was, however, 15°/min., while the analyses of the products in the present work were performed with a heating rate of only 6-8°/min. This may explain the somewhat divergent appearances of the two DTA curves.

It is also possible to discuss the factors leading to the formation of the different sulfates in the light of the structures determined together with some earlier work concerning the polymerization of zirconium and hafnium complexes in solutions. The existence of polynuclear hydrolysis products of Zr(IV) at

Table 7. Temperatures for the peaks in the DTA curves. The temperature range for the corresponding reaction is given in parentheses. (Heating rate 6-8°/min.)

Compound	H_2O-removal (°C)		SO_3-removal (°C)	
	Peaks	Ranges	Peaks	Ranges
1. $Hf(OH)_2SO_4 \cdot 2H_2O$	115, 150	(60-300)	820	(750-850)
2. $Hf(SO_4)_2 \cdot 4H_2O$	200, 300 (small)	(160-340)	770, 790	(650-800)
3. $Hf(OH)_2SO_4H_2O$	340	(280-380)	780	(700-800)
4. $Hf(OH)_2SO_4$	490 (small)	(400-520)	800	(700-820)
5. $HfO_2 \cdot 1.7SO_3 \cdot 3.1H_2O$	200, 300 (small)	(150-325)	760, 780	(670-800)

low acidities, and their depolymerization on increasing acidity, has been demonstrated by Lister and McDonald[34] with ion-exchange experiments. This effect was also found by Mark[11] in an investigation of the ZrO_2-CrO_3-H_2O system. The more polymerized compound $Zr(OH)_2CrO_4$ was obtained at the lower acidity, i.e. 5 M CrO_3, while another phase, $Zr_4(OH)_6(CrO_4)_5H_2O$, was always formed in 10 (or higher) M CrO_3.

Johnson and Kraus[3] investigated the effect of the acidity on the degree of polymerization of Zr(IV) and Hf(IV) in chloride solutions by means of ultracentrifugation. The results reported show, in general, increasing polymerization with decreasing acidity for both zirconium and hafnium with relatively minor differences between the elements. The most marked difference found, was the greater tendency of Zr(IV) to polymerize at low acidities. The degree of polymerization was also found to increase to some extent on heating the solutions. Moreover, this effect of temperature is reflected in the solid compounds $Zr(OH)_2SO_4$ (paper V), prepared at 200°C, and $Zr_2(OH)_2(SO_4)(H_2O)_4$[14] prepared at 100°C. They contain infinite $[Zr(OH)_2]_n^{2n+}$ chains and dimeric $Zr_2(OH)_2^{6+}$ species, respectively.

From Table 1 it can be seen that the two hafnium salts, $Hf(OH)_2SO_4H_2O$ and $Hf(OH)_2SO_4$, with the same degree of polymerization, are prepared at the same acidity (2 M H_2SO_4) but the latter compound requires a higher temperature for its formation. In this salt the polyhedron chains (cf. Fig. 3) are connected by sulfate groups in two directions, while in $Hf(OH)_2SO_4H_2O$ the bipyramid chains are linked in one direction only, and the layers thus obtained are held together merely by hydrogen and van der Waals bonds. In this case the condensation increased with increasing temperature only.

In view of the reported effects of acidity and temperature on polymerization, one might make the prediction that product No. 10 in Table 1, formulated as $Hf(OH)_2SO_4 \cdot 2H_2O$, ought at least to be a dimer, while No. 17, $HfO_2 \cdot 1.7SO_3 \cdot 3H_2O$, ought to be more polymerized owing to the temperature. On the other hand, the more acid solution may have caused some of the hydroxide groups to be displaced by sulfate ions.

The rather acid solution and the low temperature required for the formation of the compound formulated as $Hf(SO_4)_2 \cdot 4H_2O$ indicate no polymerization at all. However, structures reported for zirconium compounds of corresponding formula, with a sulfate to zirconium ratio 2, contain layers $(Zr(SO_4)_2 \cdot 4H_2O)$[18] as well as dimeric groups (α- and β-$Zr(SO_4)_2 \cdot 5H_2O$)[32] and these are all prepared at low temperatures. Some sort of sulfate bridges, similar to those in these structures, are thus most likely to exist in $Hf(SO_4)_2 \cdot 4H_2O$.

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